

*Investigation into the Imbibition Exhibited by some Shellac
Derivatives.*

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If shellac is boiled up with carbonate of soda, and the solution allowed to cool, a considerable part of the shellac separates out as a solid cake, resembling gutta-percha in appearance, and easily cut with a knife. If slices of this cake, or portions of the thin film deposited on the sides of the beaker, are placed in water, they rapidly expand, at the same time changing in appearance, becoming opaque, and of a weak purple colour. The colour is doubtless due to the dye which the shellac still contains. Ultimately, after swelling to several times the original size, the whole mass begins to break down into a flocculent precipitate. The time when this occurs is somewhat irregular, and seems to depend upon the conditions of preparation. If a small portion is cut from the solid cake and immersed in water and allowed to expand, and then replaced in strong carbonate of soda solution, it rapidly contracts; on being replaced in water expands again, and so can be alternately expanded and contracted.

In order to make a rough measure of the expansion of these fragments small glass cells were laid on graph paper, and a series of fragments cut so as to measure five-tenths of an inch each way, and roughly about one-tenth to two-tenths of an inch thick, were placed in these cells, which were then filled with sodium carbonate solution of different strengths, and the expansion of the fragments measured by means of the graph tracing cloth. The following results were obtained:—

Table I.

Strength of soda solution.	Original area.	New area.	Expansion in tenths of an inch.
4 normal	25	25	0
2 "	25	25	0
1 "	25	30	5
0·5 "	25	36	11
0·25 "	25	49	24
Pure water	25	81	56

These results will be found to plot into a fairly regular curve. In the case of the water, the 0·25 and the 0·5 solutions, the cakes, after expanding

to the registered size, began to break down. In the case of the normal solution, no such breaking down took place. The original strength of solution in which the shellac had been dissolved was twice normal, but had become concentrated during the solution. The shellac dissolved in potassium carbonate seemed to behave in the same way, and there was no obvious distinction between the two salts. If pieces of shellac are left for some days in a cold twice normal solution of sodium carbonate they darken in colour, but otherwise there is little alteration. If placed in water they will absorb water and expand just as in the case of the other preparation, though more slowly.

The next experiments were made with a preparation of shellac in borax, as it was found that on expansion in water the borax compound resisted disintegration, a skeleton being left retaining the shape of the original fragment. After experiments made with solutions of different strength, the following method of preparation was adopted:—57 grm. of shellac were gradually added to 100 c.c. of a solution of borax containing 8 grm. of borax. As the shellac dissolved the whole mass was continually stirred, the final result being a thick treacly mixture. The boiling of this was continued until on dropping a portion into cold water it expanded, but did not disintegrate. This preparation differs from the sodium carbonate one in that the whole of the solution is involved, there being no separation of the solid body from the liquid.

If a little of the hot mixture is poured on a glass plate and another glass plate pressed upon the top, it can be pressed out into thin sheets which readily separate from the glass when cold. Portions from these thin sheets expand when placed in water, and at the same time the water becomes stained, of a brownish yellow colour, the ultimate result being an insoluble skeleton, and a brown coloured solution out of which, on addition of an acid, the shellac is precipitated. If these squares are introduced into salt solutions of different strength they will expand up to a certain limit, depending on the strength of the salt solution, and at the same time the salt solution becomes slightly stained with the soluble compound.

The following Table, obtained by the expansion of small squares, while not to be regarded as of quantitative value, gives a sufficiently accurate indication of the nature of this process.

It was found in practice that no two preparations expanded to exactly the same extent, and that also the amount of expansion varied according to the length of time between the preparation and the use of the substance. The substance evidently loses water quickly by evaporation at ordinary temperatures, as the thin sheets rapidly curl up, and, as it loses water, it becomes less capable of expansion.

Table II.

Strength of salt solution.	Sodium sulphate.	Sodium chloride.	Ammonium acetate.
W.	55	49	49
$\frac{1}{8}$ N.	40	36	33
$\frac{1}{4}$ N.	33	30	30
$\frac{1}{2}$ N.	25	25	25
N.	25	25	25

It will be noted, for instance, in the figures given, that the final expansions of water are somewhat irregular. At the same time, the general indications are in favour of the hypothesis that we are dealing here with something of the nature of an osmotic expansion, which is controlled by the strength of the salt solution, the results being similar for different salts.

With a view to obtaining more exact results, a new method was used in the next experiments. A series of 5 c.c. glass measuring vessels were taken, and a series of brass rods about $\frac{1}{8}$ inch in diameter. Brass instead of glass was selected, because it was found that the substance which it was desired to examine clings better to a metal surface. The volume of the brass rods up to a mark having been determined by lowering them into the graduated vessels, they were then coated with a thin layer of the mixture, and placed in the vessels hanging from corks, and the displacement volume again noted. In this way a rough determination of the volume of the shellac mixture was made. Expansion was then allowed to proceed, and the rods lifted out from time to time, and the volume of liquid remaining noted. As in the former cases, considerable irregularities were found in individual experiments, but these irregularities tend to disappear when the means of separate experiments are taken.

The following Table contains the mean of the three results obtained for sodium sulphate and the three results for potassium chloride.

Table III.—Table of Results with Brass Rods. The Total Volume of the Shellac Preparation being taken as 1.

Strength of salt solution.	Mean of three measurements for sodium sulphate.	Potassium chloride.
N.	1	1
$\frac{1}{2}$ N.	1.2	1.2
$\frac{1}{4}$ N.	1.7	1.8
$\frac{1}{8}$ N.	2.0	2.1
W.	2.4	2.3

If the order of sodium sulphate and potassium chloride is remembered in the Lyotrope series, it is evident that this substance behaves quite differently to gelatine.

It will be seen how closely they agree, and how much they confirm the results from the expansion of the small squares. In one of these experiments, the expanded rod taken from one-eighth normal solution was placed in a normal solution, which was occasionally renewed. In course of a week it had contracted, the solution having increased in volume to within 15 per cent. of the original water absorbed, so that, as in the case of the other experiments earlier described, it is possible to expand in a weak, and to contract and remove water in a strong solution. If, however, instead of taking the substance expanded in a salt solution, we take the ultimate results of expansion in water, it is impossible to get this substance to contract on putting into a salt solution.

In order to get over the irregularities caused by this method of preparation, it was decided to prepare the borax solution in another way. A solution of borax was prepared containing 10 grm. in 500 c.c. borax, and shellac was added to the boiling liquid until no more dissolved. In this case, owing to the greater dilution of the borax solution, the process did not go on sufficiently far to obtain the thick mixture of the other method. This borax solution was then filtered and evaporated down, and when a thick consistency was obtained it could be poured out and cast into sheets or into any other convenient form. These sheets are very similar in appearance to those already described but are no longer affected to the same extent by being kept in the air, and show greater regularity of expansion. They are at the same time more sensitive to expansion than the substance prepared in the former way, which contains a larger proportion of shellac, and consequently an expansion begins in a solution of twice normal, although it is, at that saturation, very slight. The general form of the curve obtained agrees with that in the earlier experiments, but the breakdown of the material and free delivery to the solution of the soluble contents takes place at about $\frac{1}{8}$ to $\frac{1}{4}$ normal.

It is evident that these phenomena are of the nature of those classified under the head of imbibition which are to be noticed in the case of substances like gelatine and gum tragacanth, but at the same time there are indications that there are differences from those already recorded for gelatine. As is well known, the connection between the expansion of gelatine and water and the strength of the surrounding salt solutions is very complicated, and is not in any way proportional to the strength of the solution.

In the case of this preparation of shellac there are, I think, distinct indications that such a classification is possible. If we imagine that we are

dealing with a soluble organic molecule surrounded by a diaphragm which is impermeable to the soluble organic nucleus, and which is at the same time elastic and capable of expansion, the easiest way to explain the results is to assume the diaphragm to be also impermeable to the salt molecules. Then, as soon as the internal osmotic pressure produced by the passage of the water into the nucleus is sufficient to balance the resistance of the elastic wall plus the external osmotic pressure of the salt solution, the equilibrium is obtained and the expansion and contraction can be varied according to the strength of the external solution. If, however, the substance is introduced into pure water, the expansion goes on indefinitely until the osmotic cell walls are broken, and the soluble constituent escapes into the water. At the same time, even in the case of a salt solution, some of the external osmotic cells are probably broken, and hence some of the soluble contents escape, the percentage of the soluble content being, however, very small in the case of a salt solution as compared with the complete disintegration that takes place in the presence of water.

To test this theory a brass rod was lowered into a burette containing 15 c.c. of 0.56 N sodium sulphate. The volume of the rod up to the scratch as measured by displacement = 1.9 c.c. Rod coated with shellac preparation = 2.35 c.c.

After the shellac had finished expanding it was removed from the solution, the volume diminishing by 3.95 c.c. Therefore the volume of solution removed = 1.6 c.c. On analysis the original solution contained 0.09156 gm. sodium sulphate per cubic centimetre. After the experiment it contained 0.09232 gm. per cubic centimetre.

There was, therefore, a slight concentration of the solution due to the absorption by the shellac, the shellac taking up 0.0852 gm. per cubic centimetre instead of 0.0916 gm. It is evident, therefore, that the diaphragm is not impermeable to salt solutions.

It is evident from these experiments that the explanation of the control of the expansion of this substance is not to be found in a balance of osmotic pressure, and must be looked for elsewhere.

Now if a solution of the soluble nucleus is prepared by allowing several pieces to expand to their full in cold water and filtering off the skeleton, and a strong salt solution is added to this, the soluble matter is at once precipitated. This is not like the precipitation of colloids by very weak salt solution. The solution has to be strong, approaching saturation, to produce such a precipitate. When diluted little or no precipitation occurs. The explanation, therefore, of the control of the expansion by the strength of the salt solution seems to lie in this.

As the salt molecule passes freely through the diaphragm the soluble nucleus is dissolving in the presence of the salt solution, and therefore the amount that can dissolve and the consequent osmotic pressure is thus controlled.

Among a fair number of ordinary salts tried, only two exceptions have so far been found. In sodium carbonate the borax mixture swells much more than in water ultimately disintegrating, and ammonium chloride, even if dilute, precipitates the soluble portion. A systematic investigation of the behaviour of salts requires to be made.

At first sight the behaviour of this substance seems to differ very markedly from the behaviour of substances like gelatine and gum tragacanth, but the insolubility of the soluble portion in strong salt solutions very largely explains this difference.

In order to make a fair comparison, a medium must be used, containing a constituent in which gum tragacanth, for instance, is insoluble. The following experiment illustrates this:—

We took a series of graduated glass cylinders, and placed 0·2 grm. of powdered gum tragacanth in the bottom of each, and filled up each cylinder with 5 c.c. of a mixture of alcohol and water. The following Table gives the expansion of the gum tragacanth:—

0·2 grm. of Gum Tragacanth in 5 c.c. Solution.

	Space occupied by expanded gum.
	c.c.
90 per cent. alcohol	0·5
25 per cent. of water by volume	0·8
50 " " " "	1·4
75 " " " "	2·5
Water	3

It is here behaving in exactly the same way as the shellac mixture, but there is this difference: on replacing the weaker by stronger alcohol, it did not contract again. The interest of these experiments in shellac, in the light of the accepted view of the two-phase character of gelatine solutions and the continuance of this in the solid, and the view held as to a soluble nucleus surrounded by a network of less soluble material, is obvious.

If the shellac mixture, prepared in the way first described, is soaked for a considerable time in ether, a small quantity of a resin is extracted, but it retains its properties. Solution in alcohol and subsequent evaporation has no effect on it, and the skeleton left dissolves on raising the temperature, while the soluble portion, if evaporated down again, expands when put in

water. In the case of the preparation with sodium carbonate, as already stated, the ultimate result is complete disintegration, most passing into solution with a slight amount of flocculent precipitate.

Determinations of the heat of imbibition of the shellac derivative were made by mixing in a calorimeter 5 grm. of the ground shellac derivative with 10 c.c. of water, and noting the change of temperature. No change in temperature was recorded. Of course, this does not preclude the possibility of heat being developed by the imbibition. The heat so developed might be counterbalanced by a lowering of temperature due to the solution of the inorganic portion in the water.

In conclusion, this preparation of shellac seems to be of interest as throwing fresh light on the behaviour in presence of water of substances of the nature of gelatine and gum tragacanth, and also may possibly throw further light on the problems connected with the movements of sap.
